

19 FEDERAL REPUBLIC OF
GERMANY

GERMAN PATENT
AND TRADEMARK
OFFICE

12 Disclosure specification

10 DE 199 12 418 A1

21 File number: 199 12 418.3

22 Application date: 3/19/1999

43 Disclosure date: 9/21/2000

51 Int. Cl.⁷:

C 07 C 29/132

C 07 C 41/03

C 07 C 2/08

C 07 C 31/02

C 07 C 43/13

C 07 C 11/00

C 07 C 27/22

C 07 C 303/24

C 07 F 9/09

C 08 B 1/00

C 07 H 1/00

C 11 D 1/72

//C07H 15/04, 13/04, C07C 45/50

71 Applicant:
BASF AG, 67063 Ludwigshafen, DE

74 Representative:
Patent attorneys and attorneys at law
Bardehle, Pagenberg, Dost, Altenburg,
Geissler, Isenbruck, 68166, Mannheim

72 Inventor:
Maas, Heiko, Dr., 67105 Schifferstadt, DE;
Röper, Michael, Prof., 67157 Wacherheim,
DE; Walter, Marc, Dr., 67227 Frankenthal,
DE; Schulz, Ralf, Dr., 67346 Speyer, DE;
Tropsch, Jürgen, Dr., 67354 Römerberg, DE
Jäger, Hans-Ulrich, Dr., 67434 Neustadt,
DE;

The following information was taken from the documents filed by the applicant

54 A method for the production of tenside alcohols and tenside alcohol ethers, the manufactured products and their use.

57 This document describes a method for the production of tenside alcohols and tenside alcohol ethers that are - among other uses - very well suited as tensides or for the production of tensides. In that regard and based on olefin mixtures with a defined minimum content of linear hexenes, mixture with a dominant percentage content of branched dodecene are produced and subsequently derivatized to form tenside alcohols and are then possibly alkoxylated.

The tenside alcohol mixture obtained with the method exhibits a degree of branching of between 2.0 and 3.0 and exhibits in particular advantageous properties regarding ecotoxicity and biodegradability.

Also described here is the use of the tenside alcohols and tenside alcohol ethers to form tensides by way of glycosidation or poly-glycosidation, sulfation or phosphorylation.

DE 199 12 418 A1

Description

This invention concerns a method for the production of tenside alcohols and tenside alcohol ethers that, among other uses, are very well suited as tensides or for the production of tensides. In that regard and based on olefin mixtures with a defined minimum content of linear hexenes, mixtures with a dominant percentage content of branched dodecenes are produced that are then derivatized to form tenside alcohols and the mixtures may then be alkoxylated.

Furthermore, the invention concerns the use of tenside alcohols and tenside alcohol ethers for the manufacture of tensides through glycosidation or poly-glycosidation, sulfation or phosphorylation.

Fatty alcohols with chain lengths of between C_8 and C_{18} are used to produce non-ionic tensides. These are then reacted with alkylene oxides to form the respective fatty alcohol ethoxylates (Chapter 2.3 in: Kosswig/Stache. "The Tensides", Carl Hanser Verlag, Munich, Vienna (1993). In that respect, the chain length of the fatty alcohol affects different properties of the tenside such as wetting power, foam formation, fat removal power and cleaning power.

Fatty alcohols with chain lengths of between C_8 and C_{18} can also be used to prepare anionic tensides such as alkyl phosphates and alkyl ether phosphates. It is also possible to produce the respective sulfates in place of the phosphates (Chapter 22 in: Kosswig/Stache. "The Tensides", Carl Hanser Verlag, Munich, Vienna (1993).

Such fatty alcohols are available from natural sources such as fats and oils; they can also be produced synthetically from building blocks with a low number of carbon atoms. In that regard, the dimerization of an olefin to form a product with double the number of carbon atoms and its functionalization to form an alcohol represents one variant.

Linear olefins of a suitable chain length can be produced mainly with two methods:

In addition to paraffins, olefin isomer mixtures occur as coupler products during the Fischer-Tropsch synthesis.

Ethylene oligomerization has established itself as a further source for the manufacture of suitable olefins on an industrial scale. In that respect, aluminum alkyl catalysts as well as homogeneous nickel catalysts used in the known SHOP process of the firm Shell can be used (Weissermel/Arpe, Industrial Organic Chemistry).

Olefin fractions of a suitable chain length are processed further to form tenside alcohols. The use of ethylene has the disadvantage of a high material cost for the monomer modules. Accordingly, the use of ethylene as the raw material is economically unfeasible.

A number of processes are known for the olefin dimerization. The reaction can be run on a heterogeneous cobalt oxide/carbon catalyst (FR-A-1 403 273), in the presence of acids such as

sulfuric or phosphoric acid (FR 964 922), catalyzed with aluminum alkyl (WO 97/16398) or with a homogeneously dissolved nickel complex catalyst (US-A-4 069 273). According to the data indicated in US-A-4 069 273), the use of these nickel complex catalysts produces high-grade linear olefins with a high percentage content of dimerization products, in which case the complexing agents consist of 1,5-cyclo-octadiene or 1,1,1,5,5,5-hexafluoropentane-2,4-dione.

A dimerization of methyl pentene catalyzed with Lewis acids is described in FR-A-1 274 529, in which case boron trifluoride is used as the Lewis acid. This method is burdened with the disadvantage that it is difficult to separate the catalyst from the reaction product. This results not only in products that are contaminated with catalyst residues, but also in a significant catalyst loss.

The olefin functionalization to form alcohols while expanding the carbon structure around a C-atom is achieved appropriately with a hydroformylation reaction that yields a mixture of aldehydes and alcohols that can then be hydrated to form alcohols. Approximately 7 million tons of this product are produced annually and worldwide with the hydroformylation of olefins. A summary of catalysts and reaction conditions for the hydroformylation process is given, for example, in Beller et al. in the Journal of Molecular Catalysis, A104 (1995), 17-85 and also in Ullmanns Encyclopedia of Industrial Chemistry, Vol. A5 (1986), page 217 and following, page 333, as well as in the related references.

It is known from WO 98/23566 that sulfates, alkoxylates, alkoxy sulfates and carboxylates of a mixture of branched alkanols (oxo-alcohols) have a good surface activity level in cold water and also have a good bio-degradability. The alkanols of the applied mixture have a chain length of more than 8 carbon atoms and they exhibit on average of between 0.7 and 3 branchings. The alkanol mixture may be produced, for example, through a hydroformylation from mixtures of branched olefins that themselves may be obtained through a skeleton isomerization or through a dimerization of internal linear olefins.

The process has the advantage that the production of the dimerization feed does not require a C₃- or C₄-olefin flow. From this may be concluded that the olefins subjected to the dimerization must consist of ethylene according to the existing prior art (e.g., the SHOP process). Since ethylene is a relatively expensive base material for the tenside production, processes based on ethylene are economically less feasible than processes based on C₃- and/or C₄-flows.

The structure of the components found in the oxo-alcohol mixture is a function of the olefin mixture type that is subjected to the hydroformylation. Olefin mixtures that have been obtained through a skeleton isomerization from alpha-olefin mixtures lead to alkanols that are branched mainly at the ends of the main chain, i.e., in positions 2 and 3 calculated from the respective lobe ends (page 56, last section).

From the alcohol mixtures, the surface-active end products are prepared either by oxidizing the -CH₂OH-group to form a carboxyl group or by sulfating the alkanols or their alkoxylates.

Similar methods for the production of tensides are described in the PCT patent application WO 97/38957 and in EP-A-787 704. An alpha-olefin is also dimerized in the method described there to form a mixture consisting mainly of vinyl-idene-branched olefin dimers.

/chemical formula/

The vinyl idene compounds are then isomerized in a double-bond manner - and the double-bond thus migrates further to the center - and are then exposed to a hydroformylation to form an oxo-alcohol mixture. This is then reacted further to form tensides, e.g., by way of sulfation. A grave disadvantage of this method consists in the fact that it is based on alpha-olefins. Alpha-olefins may be produced, for example, through an oligomerization of ethylene catalyzed on a transition metal, a Ziegler build-up reaction, wax-cracking or Fischer-Tropsch process, and are thus considered relatively expensive raw materials for the tenside production. A further substantial disadvantage of this known process to produce tensides consists in the fact that a skeleton isomerization must be included between the dimerization of the alpha-olefins and the hydroformylation of the dimerization product, when one wishes to obtain mainly branched products. Based on the need to use a raw material that is relatively expensive for the tenside production and the need to include an additional process step, i.e., the isomerization, this known method becomes substantially disadvantageous with respect to economics.

US-A-5,780,694 describes the production and use of alcohols with branching degrees of between 0.9 and 2. The alcohols are produced with a homogeneously catalyzed dimerization of internal olefins and a subsequent hydroformylation, in which case the n-percentage content exceeds 85% by weight in the olefin to be dimerized. A particular advantage of these alcohols consists in the cold water behavior of their sulfates. This document contains no information on the properties of the respective ethoxylates and their sulfates. The fact that the alcohol production does not require olefin mixtures that contain propene or butene, but is based on mixtures that contain at least 85% by weight C₆ to C₁₀-olefins, is mentioned as a further advantage of this method.

The production of tridecanol mixtures with the dimerization of so-called "dimer propene" and a following hydroformylation of the dodecene mixture is described in the parallel patent application 198 59 911.0. It typically contains less than 30% by weight of linear hexenes. The "dimer propene" used for this method consists of a hexene isomer mixture that is obtained in refinery processes during the propene oligomerization according to the DIMERSOL method, for example (see Cornils/Hermann, Applied Homogeneous Catalysis, Verlag Chemie (1996)).

Olefin mixtures produced with a dimerization of C₃/C₄-sections or C₄-fractions according to the DIMERSOL process are suitable initial materials for this method. However, the ratio between ecotoxicity and biodegradability has not yet reached an optimal level.

The disadvantages described for the prior art and particularly the need to reduce cost points to the task to present a method for the production of tenside alcohols with application-technical advantages, with which the use of expensive raw materials, and particularly of expensive ethylene can be avoided.

In a surprising manner, it was now found that the production of branched olefins and alcohols (oxo-alcohols) that are easy to process further to form effective tensides - hereinafter called "tenside alcohols" - and that exhibit an advantageous combination of favorable properties regarding their manufacture and further processing and particularly in view of their eco-toxicity and bio-degradability is possible when one proceeds according to the method in accordance with the invention and described in the following.

An object of this invention also consists in a method for the production of tenside alcohols that have particularly advantageous properties regarding ecotoxicity and biodegradability and of tenside alcohol ethers through

- a) a dimerization of olefin mixtures,
- b) a derivatization to form primary alcohols and
- c) a possibly following alkoxylation,

characterized by the fact that the olefin mixture to be used contains between 30 and 80% by weight of linear hexene isomers and at least 60% by weight hexene isomers as a whole.

Accordingly, the olefin mixture used for the method in accordance with the invention must meet two conditions:

1. The sum of all hexene isomers contained in it, i.e., the linear and branched hexene isomers, must amount to least 60% by weight and
2. the sum of the linear hexene isomers contained in it must vary between 30 and 80% by weight.

It was shown that products with very favorable overall properties can be obtained in a particularly economical manner with the method in accordance with the invention, when the olefin mixture to be used is obtained by mixing dimer propene and linear hexene at a weight ratio of between 0.3:1 and 1:0.1.

An olefin mixture consisting of a mixture of dimer propene and linear hexene at a weight ratio of between 0.5:1 and 1:0.5 is particularly preferred for use in the method in accordance with the invention.

With the dimerization of the hexene isomer mixtures (step a) in the method in accordance with the invention), dimerization products are obtained that - in view of the further processing to form tenside alcohols - exhibit particularly favorable components and particularly favorable compositions, when one uses a dimerization catalyst that contains at least one element of the secondary group VIII in the periodic table of elements, and the catalyst composition and the reaction conditions are selected in such a manner that a dimer mixture containing less than 10% by weight of compounds that have a structural element of the formula 1 (vinyl idene group) are obtained

/formula/

where A¹ and A² are aliphatic hydrocarbon residues.

The dimerization can be performed in a homogeneously or heterogeneously catalyzed manner. Preference is hereby given to the heterogenous process, since this simplifies the catalyst separation and the method thus becomes more economical and no sewage water that damages the environment is produced, i.e., unlike the sewage water that is generally produced when dissolved catalysts are separated by hydrolysis, for example. A further advantage of the heterogeneous method

consists in the fact that the dimerization product does not contain halogens and particularly contains no chlorine or fluorine. Homogeneously dissolving catalysts generally contain ligands with halogenide or they are used in combination with halogen-containing co-catalysts. From such catalyst systems, halogen can be introduced into the dimerization products and this has a substantially negative effect on the product quality as well as on the further processing and particularly on the hydroformylation to form tenside alcohols.

The heterogeneous catalysis is performed appropriately with combinations of oxides of metals from the secondary group VIII with aluminum oxide on carrier materials consisting of silicon oxides and titanium oxides like those known from DE-A-43 39 713. The heterogeneous catalyst can be used on a solid bed - and then preferably in a large-grained form as a 1 mm to 1.5 mm grit - or suspended (particle size between 0.05 and 0.5 mm). In the heterogeneous form, the dimerization is run appropriately in a closed system at temperatures of between 80 and 200 °C, preferably at between 100 and 180 °C, and under the pressure occurring at the reaction pressure and possibly under a protective gas overpressure. To achieve optimal reaction rates, a reaction mixture is circulated several times, in which case a certain percentage content of the circulated product is removed and replaced with the raw material.

In the dimerization in accordance with the invention, one obtains mixtures of simple unsaturated hydrocarbons, most of whose components exhibit a chain length that is twice as long as that of the initial olefins.

The dimerization catalysts and the reaction conditions are selected appropriately within the scope of the above information in such a manner that the olefin mixtures produced in accordance with the invention have a high percentage content of linear olefins, generally above 85% and particularly above 90%. Another characteristic consists in the fact that mainly groups with (y-4) and (y-5) C-atoms are bonded at the branching points of the main chain, in which case "y" represents the number of carbon atoms of the monomers used for the dimerization. The value (y-5)=0 indicates that there is no lateral chain.

For C₁₂-olefin mixtures produced in accordance with the invention, the main chain preferably carries methyl or ethyl groups at the branching points.

It was also determined that the dimerization mixtures are particularly easy to derivatize further when the position of the double-bond meets certain requirements. In these advantageous olefin mixtures, the position of the double-bonds in relation to the branchings is characterized by the fact that the ratio between the "aliphatic" hydrogen atoms and the "olefinic" hydrogen atoms varies in the range of $H_{\text{aliphatic}} : H_{\text{olefinic}} = 47:1$ to $11:1$, in which case n represents the carbon atom number of the olefin obtained with the dimerization.

("Aliphatic" hydrogen atoms are considered those bonded to carbon atoms that do not participate at any C=C double-bond (Pi bond), while "olefinic" hydrogen atoms are considered those bonded to a carbon atom that activates a Pi-bond).

Particularly preferred are dimerization mixtures with the following $H_{\text{aliphatic}} : H_{\text{olefinic}}$ ratio: 23:1 to 14:1.

The new olefin mixtures that can be obtained with the first step of the method in accordance with the invention and that exhibit the above-mentioned structure are also an object of this invention. They are valuable intermediate products, particularly for the further steps of the method in accordance with the invention, i.e., the production of branched primary alcohols and tensides that is described later; however, they can also be used in other industrial processes that are based on olefins, particularly in the case that the end products are expected to exhibit an improved biodegradability.

When the olefin mixtures in accordance with the invention are used for the production of tensides according to step b) of the method in accordance with the invention, they are initially and in a basically known manner derivatized to form tenside alcohols.

This can be achieved in different ways, including the direct or indirect addition of water (hydration) on the double-bond or an addition of CO and hydrogen (hydroformylation) on the $C=C$ =double-bond.

The hydration of the olefins obtained with process step c) is achieved appropriately with a direct addition of water under a proton catalysis. It is only natural that this can be achieved as well in an indirect manner such as the addition of a high-percentage sulfuric acid to an alkanol sulfate and a subsequent saponification to form an alkanol. The more appropriate direct water addition is performed in the presence of acid and particularly heterogeneous catalysts and generally at the highest-possible partial olefin pressure and at the lowest-possible temperatures. Particularly phosphoric acid on carriers such as SiO_2 or celite and also acid ion-exchangers have proven themselves as catalysts. Selecting the conditions is a function of the reactivity of the olefins to be reacted and can be routinely determined with initial tests (Reference: e.g., A.J. Kresge et al. J.Am.Chem.Soc. 93, 4907 (1971); Houben-Weyl, Vol. 5/4(1960), pages 102-132 and 535-539). The hydration generally leads to mixtures of primary and secondary alcohols in which there are more secondary alkanols.

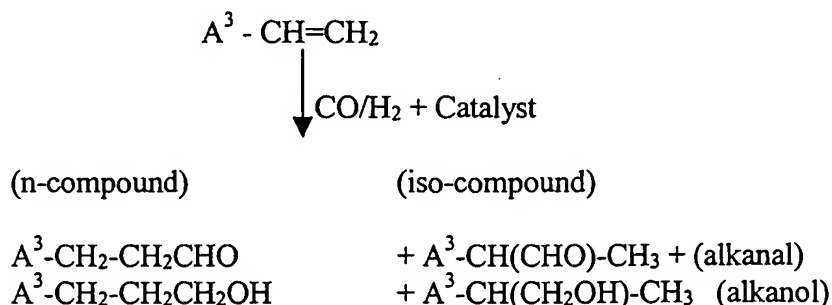
The tenside production on the basis of primary alkanols is more favorable. Accordingly, it is preferred to derivatize the olefin mixtures obtained in step c) by a reaction with carbon monoxide and hydrogen in the presence of suitable catalysts that preferably contain cobalt or rhenium and to hydroformylate them to form branched primary alcohols.

Accordingly, a further preferred object of this invention consists in a method for the production of mixtures of primary alkanols that are suitable, among other uses, for a further processing to form tensides by way of a hydroformylation of olefins and the method is characterized by the fact that the above-described olefin mixtures in accordance with the invention are used as the initial material.

A good overview for the hydroformylation method with numerous further references is found, for example, in the extensive paper written by Beller et al. in the Journal of Molecular Catalysis, A104 (1995), 17-85, or in Ullmanns Encyclopedia of Industrial Chemistry, Vol. A5 (1986), page 217 and following, page 333, as well as in the related references.

The extensive information given there permits the expert to also hydroformylate the branched

olefins in accordance with the invention. In this reaction, CO and hydrogen are deposited on olefinic double-bonds, in which case mixtures of aldehydes and alkanols are obtained according to the following reaction formula:



(A³ = hydrocarbon rest)

The mol ratio between n- and iso-compounds in the reaction mixture is a function of the selected process conditions for the hydroformylation and of the catalyst to be used and generally varies between 1:1 and 20:1. The hydroformylation is normally performed at a temperature range of between 90 and 200 °C and at a CO/H₂ pressure of between 2.5 and 35 MPa (25 to 350 bar). The mixture ratio between carbon monoxide and hydrogen is a function of the preferred product to be produced, i.e., alkanals or alkanols. The appropriate range CO:H₂ varies between 10:1 and 1:10 and preferably between 3:1 and 1:3, in which case ranges are selected for the lower partial hydrogen pressure for the production of alkanals and for the higher partial hydrogen pressure such as CO:H₂ = 1:2 for the production of alkanols.

Particularly suited catalysts consist of metal compounds of the general formula HM(CO)₄ or M₂(CO)₈, in which case M is a metal atom, preferably a cobalt, rhodium or ruthenium atom.

From the respective catalysts or initial catalyst stages used for the process, catalytically active species of the general formula H_xM_y(CO)_zL_q are generally formed under hydroformylation conditions, in which case M stands for a metal of secondary group VIII, L for a ligand that can be a phosphine, phosphite, amine, pyridine or any other donor compound - also in the form of a polymer - and q, x, y and z are whole numbers as a function of the metal valence and metal type as well as of the ligand's bonding power, in which case q can also be 0.

Metal M preferably consists of cobalt, ruthenium, rhodium, palladium, platinum, osmium or iridium or particularly preferred of cobalt, rhodium or ruthenium.

Suitable rhodium compounds or complexes consist of, for example, rhodium(II) and rhodium(III) salts such as rhodium(III) chloride, rhodium(III) nitrate, rhodium(III) sulfate, potassium rhodium sulfate, rhodium(II) or rhodium(III) carboxylate, rhodium(II) and rhodium(III) acetate, rhodium(III) oxide, salts of the rhodium(III) acid such as tris-ammonium hexachloro-rhodate-(III). Also suited are rhodium complexes such as rhodium bis-carbonyl acetyl acetonate, acetyl-acetonato bis-ethylene rhodium(I). Preference is given to rhodium bis-carbonyl acetyl acetonate or rhodium acetate.

Suitable cobalt compounds consist of, for example, cobalt(II) chloride, cobalt(II) sulfate, cobalt(II) carbonate, cobalt(II) nitrate, their amine or hydrate complexes, cobalt carboxylates such as cobalt acetate, cobalt ethyl hexanoate, cobalt naphthanoate as well as the cobalt caprolactamate complex. Carbonyl complexes of the cobalt such as di-cobalt octocarbonyl, tetra-cobalt dodecacarbonyl and hexacobalt hexadecacarbonyl can be used as well.

The compounds of cobalt, rhodium and ruthenium mentioned here are basically known and are sufficiently described in the available references or they can be prepared by an expert in a similar manner as the already known compounds.

The hydroformylation can be performed by adding inert solvents or dilution agents or without adding such agents. Suitable inert additives consist, for example, of acetone, methyl ethyl ketone, cyclo-hexanone, toluene, xylene, chlorobenzene, methylene chloride, hexane, petroleum ether, acetonitrile as well as the high-boiling percentage contents from the hydroformylation of the dimerization products.

When the aldehyde content in the obtained hydroformylation product is too high, this situation can be remedied in a simple manner with a hydration with hydrogen, for example, in the presence of Raney nickel or with the use of other catalysts that are known for their hydration reactions and contain particularly copper, zinc, cobalt, nickel, molybdenum, zircon or titanium. In that regard, most of the aldehyde percentage content will have been hydrated to alkanols. A practically complete removal of the aldehyde percentage content from the reaction mixture can be achieved, if desired, with a post-hydration with an alkali boron hydride under particularly careful and economical conditions.

The mixtures of branched primary alkanols that can be obtained with the hydroformylation of the olefin mixtures in accordance with the invention also form an object of this invention.

Non-ionic or anionic tensides can be produced in different ways from the alkanols in accordance with the invention.

Non-ionic tensides are obtained by reacting the alkanols with alkylene oxides (alkoxylation) of formula II

/Formula/ (II)

where R^1 is hydrogen or a linear or branched aliphatic residue of the formula C_nH_{2n+1} and n represents a number of between 1 and 16 and preferably of between 1 and 8. R^1 stands in particular for hydrogen, methyl or ethyl.

The alkanols in accordance with the invention can be reacted with one single alkylene oxide species or with several different ones. The alcohol reaction with the alkylene oxides forms compounds that again carry an OH-group and thus can react again with an alkaline oxide molecule. Accordingly and as a function of the mol ratio between alcohol and alkylene oxide, reaction products that have more or less long polyether chains are obtained. The polyether chains may contain between 1 and approx. 200 alkylene oxide modules. Compounds, whose polyether chains contain between 1 and 10 alkylene oxide structural components, are preferred.

The chains may consist of the same chain bonds or they may have different alkylene oxide

structural components that differ from each other with respect to their residue R^1 . These different structural components may be present within the chain in a statistical distribution or in the form of blocks.

The following reaction formula shall explain the alkoxylation of the alkanols in accordance with the invention with the example of a reaction with two different alkylene oxides that are used in two different mol quantities x and y .

/reaction formula/

alkali \longrightarrow

R^1 and R^{1a} are different residues within the scope of the definitions given above for R^1 , and R^2 -OH is a branched alkanol in accordance with the invention.

The alkoxylation is preferably catalyzed with strong bases that are added appropriately in the form of alkali hydroxides or earth alkali hydroxides, generally at a quantity of between 0.1 and 1% by weight in relation to the quantity of alkanol R^2 -OH. (See G. Gee et al., J.Chem.Soc. (1961), page 1345; B. Wojtech, Makromol. Chem. 66, (1966), page 180).

An acid catalysis of the addition reaction is also possible. In addition to Bronsted acids, it is also possible to use Lewis acids such as $AlCl_3$ or BF_3 . (See P.H. Plesch, The Chemistry of Cationic Polymerization, Pergamon Press, New York (1963).

The addition reaction is run in a closed container at temperatures of between approx. 120 and 220 °C and preferably of between 140 and 160 °C. Alkylene oxide or the mixture of different alkylene oxides is supplied to the mixture consisting of the alkanol mixture in accordance with the invention and alkali at the steam pressure of the alkylene oxide mixture that occurs at the selected reaction temperature. If desired, the alkylene oxide can be diluted with an inert gas to between approx. 30 and 60%. This provides an additional safety factor against an explosion-like poly-addition of the alkylene oxide.

The use of an alkylene oxide mixture yields the formation of polyether chains, in which the different alkylene oxide modules are distributed in a practically statistical manner. Variations in the module distribution along the polyether chain occur on the basis of different component reaction velocities and can be achieved at random by continuously adding an alkylene oxide mixture of a program-controlled composition. When the different alkylene oxides are brought to react one after the other, one obtains polyether chains with a block-like distribution of the alkylene oxide modules.

The polyether chain length in the reaction product varies statistically near a mean value that basically corresponds to the stoichiometric value obtained from the composition.

The alkoxyates that can be produced on the basis of the olefin mixtures and alkanol mixtures in accordance with the invention also form an object of this invention. They have a very good surface activity level and can thus be used in many applications as neutral tensides.

Based on the alkanol mixtures in accordance with the invention, it is also possible to produce surface-active glycosides and poly-glycosides (oligo-glycosides). These substances also exhibit very good tenside properties. They are obtained with a single or multiple reaction (glycosidation or poly-glycosidation) of the alkanol mixtures in accordance with the invention with mono-, di- or poly-saccharides with the exclusion of water and in an acid catalysis. Examples of suitable acids are HCl or H₂SO₄. Oligo-glycosides with a statistical chain length distribution are generally obtained, in which case the average degree of oligomerization varies between 1 and 3 saccharide residues.

In another standard synthesis, the saccharide is first and in an acid catalysis acetalized with a low-molecular alkanol such as butanol to form butanol glycoside. This reaction can also be performed with aqueous solutions of the saccharide. The low alkanol glycoside such as butanol glycoside is then reacted with the alkanol mixtures in accordance with the invention to form the desired glycosides in accordance with the invention. After neutralizing the acid catalysts from the equilibrium mixture, e.g., by way of a distillation in a vacuum, it will be possible to remove excess alkanols with long and short chains.

A further standard method runs by way of the O-acetyl compounds of the saccharides. With the help of halogen hydrogen that was preferably dissolved in acetic acid, these are converted into the corresponding O-acetyl halosaccharides that react in the presence of agents that bond acids with the alkanols to form the acetylated glycosides.

The glycosidation of the alcohol mixtures in accordance with the invention is preferably carried-out with mono-saccharides, i.e., hexoses such as glucose, fructose, galactose, mannose as well as the pentoses such as arabinose, xylose or ribose. Glucose is particularly preferred for the glycosidation of the alkanol mixtures in accordance with the invention. It is only natural that mixtures of the above-mentioned saccharides can be used for the glycosidation. In this case, glycosides with statistically distributed sugar residues are obtained as a function of the reaction conditions. The glycosidation can also be performed several times and poly-glycoside chains will then be deposited on the hydroxyl groups of the alkanols. With a poly-glycosidation and the use of several saccharides, the saccharide modules may be distributed statistically within the chain or may form blocks of the same modules.

One may obtain furanose or pyranose structures as a function of the selected reaction temperature. The reaction can also be performed in suitable solvent or diluting agents to improve the solubility ratios.

Standard methods and suitable reaction conditions have been described in several publications such as in "Ullmanns Encyclopedia of Industrial Chemistry", 5th edition, Vol. A25 (1994), pages 792-793 and in the references listed there, in K. Igarashi, Adv. Carbohydr.Chem.Biochem. 34, (1977), page 243-283, in Wulff and Röhle, Angew.Chem. 86 (Applied Chem. 86), (1974), page 173-187 or in Krauch and Kunz, Organic Chemistry Reactions, page 405-408, Hüthig, Heidelberg, (1976).

Glycosides and poly-glycosides (oligo-glycosides) that can be produced on the basis of olefin mixtures and alkanol mixtures in accordance with the invention also form an object of this invention.

The alkanol mixtures in accordance with the invention as well as the polyethers produced from them can be converted into anionic tensides by esterifying (sulfating) them in a generally known manner with sulfuric acid or sulfuric acid derivatives to form alkyl sulfates or alkyl ether sulfates or with phosphoric acid or its derivatives to form acid alkyl phosphates or alkyl ether phosphates.

Sulfation reactions for alcohols have been described already, e.g., in US-A-3 462 525, 3 420 875 or 3 524 964. Details on the reaction execution are found in "Ullmanns Encyclopedia of Industrial Chemistry", 5th edition, Volume A25, (1994), page 779-783 and in the references listed there.

When sulfuric acid itself is used for the esterification, it is appropriate to use between 75 and 100% by weight and preferably between 85 and 98% by weight acid (so-called "concentrated sulfuric acid" or "monohydrate"). The esterification can be performed in a solvent or diluting agent, when this is desirable to control the reaction, e.g., the heat development. The alcoholic reactant is generally provided first and the sulfation agent is added slowly under a continuous stirring. When a complete esterification of the alcohol component is desired, the sulfation agent and the alkanol are used at a mol ratio of between 1:1 and 1:1.5, preferably of between 1:1 and 1:1.2. Smaller quantities of sulfation agents may be advantageous, when mixtures from alkanol alkoxylates in accordance with the invention are to be used and combinations of neutral and anionic tensides are to be produced. The esterification is normally performed at temperatures of between room temperature and 85 °C and preferably of between 45 and 75 °C.

It may be appropriate to perform the esterification at the boiling point of and in a low-boiling solvent and diluting agent that does not mix with water, in which case water formed during the esterification shall be distilled-off in an azeotropic manner.

Instead of using sulfuric acid of the above-mentioned concentration, the sulfation of the alkanol mixtures in accordance with the invention can also be performed with sulfur trioxide, sulfur trioxide complexes, solutions of sulfur trioxide in sulfuric acid ("oleum"), chlorosulfonic acid, sulfuryl chloride or also amidosulfonic acid. The reaction conditions shall then be adjusted accordingly.

When sulfur trioxide is used as the sulfation agent, the reaction can be performed in an advantageous manner at a counterflow in a falling film reactor, possibly also continuously.

The quantities are neutralized after the esterification by adding alkali and are processed possibly after removing excess alkali sulfates and possibly existing solvents.

The acid alkanol sulfates and alkanol ether sulfates and their mixtures obtained after sulfating alkanols and alkanol ethers in accordance with the invention and their salts also form an object of this invention.

In an analogous manner, alkanols and alkanol ethers in accordance with the invention and their mixtures can be reacted with phosphorylation agents to also form acid phosphoric acids (phosphated).

Suitable phosphorylation agents largely consist of phosphoric acid, poly-phosphoric acid and phosphorus pentoxide as well as POCl_3 , when this is followed by a hydrolysis of the remaining acid chloride functions. The alcohol phosphorylation is described, for example, in Synthesis 1985, pages 449 to 488.

The acid alkanol phosphates and alkanol ether phosphates obtained with the phosphorylation of alkanols and alkanol ethers in accordance with the invention and their mixtures also form an object of this invention.

Finally, the use as tensides of alkanol ether mixtures, alkanol glycosides as well as the acid sulfates and phosphates of the alkanol mixtures and the alkanol ether mixtures that can be produced with the olefin mixtures in accordance with the invention also forms an object of the invention.

The following examples explain the production and use of the tensides in accordance with the invention.

Example 1

Heterogeneously catalyzed dimerization of hexene isomer mixtures

A rotating stirrer autoclave with a capacity of 2.5 liters was filled with 200 ml of a catalyst with the composition indicated below:

50% by weight NiO , 34% by weight SiO_2 , 13% by weight TiO_2 , 3% by weight Al_2O_3 (conditioned for 24 hours in N_2 at 160 °C, used in the form of a powder).

A quantity of 500 g 1-hexene and 500 g dimer propene consisting of 23% by weight n-hexene, 70% by weight methyl pentene and 7% by weight dimethyl butene was added and reacted for 10 h at 150 °C.

The thus obtained reaction product was processed by distillation and a fraction consisting of 99% by weight dodecene was isolated. It had an ISO-index of 2.1 (4.1 methyl groups/molecule were measured after the olefin hydration using ^1H -NMR spectroscopy) and the ratio between aliphatic and olefinic protons was 14.7:1.

Example 2

Hydroformylation of the dodecene mixture in accordance with the invention

A quantity of 750 g of the olefin mixture produced according to example 1 was hydroformylated for 7.5 hours with 2.94 g $\text{Co}_2(\text{CO})_8$ at 185 °C and at 280 bar CO/H_2 (volume ratio = 1 : 1) while adding 75 g H_2O in a lifting stirrer autoclave with a capacity of 2.5 liters. The reaction discharge was de-cobalted in an oxidative manner with 10% by weight acetic acid at 90 °C and with the introduction of air. While adding 10% by weight water, the oxo-product was hydrated in a 2.5 l tube reactor with the dripping method on a Co/Mo solid bed at 175 °C and at a hydrogen pressure of 280 bar. The alcohol mixture was processed by distillation. The OH-number of the obtained tri-decanol fraction was 273 KOH/g. The ^1H -NMR-spectroscopy established the presence of 3.5 methyl groups/molecule, corresponding to an average branching degree of 2.5.

Example 3

Fatty alcohol ethoxylate with 7 mol ethylene oxide

A quantity of 400 g of the alkanol mixture produced in accordance with example 2 was filled into a dry 2 l autoclave with 1.5 g NaOH. The autoclave content was heated to 150 °C and 616 g ethylene oxide was filled under pressure into the autoclave. After the whole ethylene oxide quantity had been filled in the autoclave, the autoclave was maintained at 150 °C for 30 minutes. The catalyst was neutralized by adding sulfuric acid after the cooling phase.

The thus obtained ethoxylate represented a neutral tenside. It had a cloud point of 72 °C as measured according to DIN 53917, 1% by weight in 10% by weight of an aqueous butyl di-glycol solution. The surface tension of a solution of 1 g/l of the substance in water was 25.8 mN/m, measured according to DIN 53914.

Example 4

Fatty alcohol ethoxylate with 3 mol ethylene oxide

A quantity of 600 g of the alkanol mixture produced in accordance with example 2 was filled into a dry 2 l autoclave with 1.5 g NaOH. The autoclave content was heated to 150 °C and 396 g ethylene oxide was filled under pressure into the autoclave. After the whole ethylene oxide quantity had been filled in the autoclave, the autoclave was maintained at 150 °C for 30 minutes. The catalyst was neutralized by adding sulfuric acid after the cooling phase.

The thus obtained ethoxylate represented a neutral tenside. It had a cloud point of 42.1 °C as measured according to DIN 53917, 1% by weight in 10% by weight of an aqueous butyl di-glycol solution. The surface tension of a solution of 1 g/l of the substance in water was 26.1 mN/m, measured according to DIN 53914.

Example 5

Alkyl phosphate

A quantity of 300 g of the alcohol mixture produced in accordance with example 2 was heated in a stirrer tank and in nitrogen to 60 °C and was reacted slowly with 125 g poly-phosphoric acid. In that regard, the temperature shall not exceed 65 °C. Toward the end of the adding phase, the mixture was heated to 70 °C and was stirred further for one hour at this temperature.

The thus obtained product represented an anionic tenside. At a concentration of 1 g/l, an aqueous solution of the substance in water exhibited a surface tension of 28.4 mN/m, measured according to DIN 53914.

Example 6

Alkyl ether phosphate

A quantity of 560 g of the fatty alcohol ethoxylate mixture produced in accordance with example 4 was heated to 60 °C in a stirrer tank and in nitrogen and was reacted slowly with 92 g poly-phosphoric acid. In that regard, the temperature shall not exceed 65 °C. Toward the end of the adding phase, the mixture was heated to 70 °C and was stirred further for one hour at this temperature. The thus obtained product represented an anionic tenside. At a concentration of 1 g/l, an aqueous solution of the substance in water exhibited a surface tension of 35.2 mN/m, measured according to DIN 53914.

Example 7

Alkyl sulfate

A quantity of 190 g of the tridecanol mixture produced in accordance with example 2 was heated to 60 °C in a stirrer tank and in nitrogen and was reacted slowly with 98 g sulfuric acid. In that regard, the temperature should not exceed 65 °C. Toward the end of the adding phase, the mixture was heated to 70 °C and was stirred further for one hour at this temperature.

The thus obtained product represented an anionic tenside. At a concentration of 1 g/l, an aqueous solution of the substance in water exhibited a surface tension of 28.9 mN/m, measured according to DIN 53914.

Example 8

Alkyl ether sulfate

A quantity of 480 g of the fatty alcohol ethoxylate mixture produced in accordance with example 4 was heated to 60 °C in a stirrer tank and in nitrogen and was reacted slowly with 146 g sulfuric acid. In that regard, the temperature should not exceed 65 °C. Toward the end of the adding phase, the mixture was heated to 70 °C and was stirred further for one hour at this temperature.

The thus obtained product represented an anionic tenside. At a concentration of 1 g/l, an aqueous solution of the substance in water exhibited a surface tension of 34.9 mN/m, measured according to DIN 53914.

Patent claims

1. A method for the production of tenside alcohols that have particularly advantageous properties regarding ecotoxicity and biodegradability, and of the respective tenside alcohol ethers through

a) dimerization of olefin mixtures,

- b) derivatization to form primary alcohols and
- c) possibly following alkoxylation,

characterized by the fact that the olefin mixture to be used contains between 30 and 80% by weight of linear hexene isomers and a total of at least 60% by weight hexene isomers.

2. A method in accordance with claim 1, characterized by the fact that the hexene isomer mixture used here contains dimer propene and linear hexene at a weight ratio of between 0.3:1 and 1:0.1.

3. A method in accordance with at least one of claims 1 and 2, characterized by the fact that process step a) - the dimerization - is performed in a heterogeneous manner.

4. A method in accordance with at least one of claims 1 through 3, characterized by the fact that one uses a dimerization catalyst containing at least one element from secondary group VIII of the periodic system for elements, and that the catalyst composition and the reaction conditions are selected such that a dimer mixture that contains less than 10% by weight of compounds containing a structural element of the formula II (vinyl idene group) is obtained

/formula/

where A¹ and A² are aliphatic hydrocarbon residues.

5. Olefin mixtures that can be produced according to process step a) of the method in accordance with claim 1.

6. Olefin mixtures in accordance with claim 5, characterized by the fact that they contain a percentage content of more than 85% and particularly of more than 90% of components with branchings and a low percentage content, generally less than 15 and particularly less than 10% of linear olefins.

7. Olefin mixtures in accordance with at least one of claims 5 and 6, characterized by the fact that mainly groups with (y-4) and (y-5) C-atoms are bonded at the branching points of the main chain, in which case y is the number of carbon atoms in the monomer used for the dimerization.

8. Olefin mixtures in accordance with at least one of claims 5 through 7, characterized by the fact that the branched components of the dimerization mixture have one branching or two branchings at adjacent C-atoms at an area located at 1/4 to 3/4 and preferably at 1/3 to 2/3 of the chain length of their main chain.

9. Olefin mixtures in accordance with at least one of claims 5 through 8, characterized by the fact that mainly groups with one or two C-atoms are bonded at the branching points of the main chain.

10. Olefin mixtures in accordance with at least one of claims 5 through 9, characterized by the fact that the ratio between aliphatic and olefinic hydrogen atoms at the branched components varies over a range of $H_{\text{aliphatic}} : H_{\text{olefinic}} = 47:1$ to $11:1$, where n represents the carbon atom number of the olefin obtained with the dimerization.

11. Olefin mixtures in accordance with at least one of claims 5 through 10, characterized by the fact that the ratio between aliphatic and olefinic hydrogen atoms varies over a range of $H_{\text{aliphatic}} : H_{\text{olefinic}} = 23:1$ to $14:1$ at the branched components.

12. Tenside alcohols and their alkoxylation products that can be produced according to process steps a), b) and possibly c) of the method indicated in claim 1.

13. Tenside alcohols and their alkoxylation products in accordance with claim 12, characterized by the fact that they have a branching degree of between 2.0 and 3.0.

14. The use of the tenside alcohol alkoxylation products in accordance with claim 12 as non-ionic tensides.

15. The use of the tenside alcohols in accordance with claim 12 for the production of tensides.

16. The use of the tenside alcohols in accordance with claim 12 for the production of alkanol glycoside and poly-glycoside mixtures through a single or multiple reaction (glycosidation, polyglycosidation) with mono-, di- or poly-saccharides with the exclusion of water under an acid catalysis or with O-acetyl saccharide halides.

17. The use of the tenside alcohols and their alkoxylation products in accordance with claim 12 for the production of surface-active sulfates by esterifying them with sulfuric acid or derivatives of sulfuric acid to form acid alkyl sulfates or alkyl ether sulfates.

18. The use of the tenside alcohols and their alkoxylation products in accordance with claim 12 for the production of surface-active phosphates by esterifying them with phosphoric acid or its derivatives to form acid alkyl phosphates or alkyl ether phosphates.